Supporting Information

Organosulfates as Tracers for Secondary Organic Aerosol (SOA) Formation from 2-Methyl-3-Buten-2-ol (MBO) in the Atmosphere

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Table S1. Supporting data from BEARPEX 2007 campaign.

Start Time	average temperature (°C)	average RH (%)	average O_3 (ppb)	average organics (μg/m^3)	average [H^+] [a] (nmol/m^3)	average MBO (ppb)	MBO OS[b] (ng/m^3)	average isoprene (ppb)	IEPOX OS[b] (ng/m^3)	Fraction of MBO OS in total organics
9/20/07 18:45	7.4	89.5	29.8	3.98	0.00	0.10	0.19	0.18	1.63	0.00%
9/21/07 7:45	17.6	42.7	41.2	1.93	0.00	0.25	0.33	0.12	1.87	0.02%
9/21/07 13:15	13.3	62.7	49.8	3.10	0.24	0.40	1.26	0.28	1.23	0.04%
9/21/07 18:45	7.8	82.5	40.9	3.56	NA	0.11	0.27	0.08	0.42	0.01%
9/22/07 7:45	7.2	97.2	NA	2.62	NA	0.18	0.34	NA	1.93	0.01%
9/22/07 13:15	7.2	98.5	34.4	1.46	0.00	0.18	0.00	0.03	0.54	0.00%
9/22/07 18:45	5.4	99.2	29.1	1.53	0.37	0.05	0.00	0.02	0.60	0.00%
9/23/07 7:45	6.8	99.1	37.4	1.24	0.10	0.08	0.13	0.02	0.92	0.01%
9/23/07 13:15	9.0	88.0	34.0	1.71	0.00	0.18	0.19	0.10	1.76	0.01%
9/23/07 18:45	6.0	80.1	27.7	1.38	0.10	0.05	0.10	0.07	1.26	0.01%
9/24/07 7:45	14.5	37.0	37.8	1.39	0.43	0.18	1.05	0.04	1.10	0.08%
9/24/07 13:15	15.3	44.8	48.5	2.92	1.11	0.28	0.24	0.10	1.64	0.01%
9/24/07 18:45	7.7	68.3	41.1	2.46	1.10	0.11	0.13	0.19	2.40	0.01%
9/25/07 7:45	17.2	39.1	NA	NA	NA	0.37	1.13	NA	3.18	NA
9/25/07 13:15	18.2	37.7	NA	3.43	NA	0.40	0.89	NA	3.11	0.03%

[a] [H^+] is calculated from charge balance based on the AMS data of [SO_4^{2-}], [NO_3^-], and [NH_4^+].
[b] "OS" represents organosulfate.

Table S2. Supporting data from BEARPEX 2009 campaign.

Start Time	average temperature (°C)	average RH (%)	average O_3 (ppb)	average organics (μg/m^3)	average [H^+][a] (nmol/m^3)	average MBO (ppb)	MBO OS[b] (ng/m^3)	average isoprene (ppb)	IEPOX OS[b] (ng/m^3)	Fraction of MBO OS in total organics
7/25/09 19:15	17.8	50.3	45.1	2.42	8.64	1.54	1.39	0.61	6.44	0.06%
7/26/09 8:45	27.8	28.5	49.4	2.26	12.17	4.47	10.31	1.30	8.16	0.46%
7/26/09 14:15	27.6	30.8	64.5	3.04	14.02	6.59	25.86	2.05	10.63	0.85%
7/26/09 19:45	19.6	37.7	51.3	2.16	5.93	1.99	2.18	0.96	8.44	0.10%
7/27/09 8:45	29.4	24.5	54.3	1.95	7.70	5.77	6.59	1.59	9.66	0.34%
7/27/09 14:15	28.9	26.3	70.1	3.18	15.40	5.81	20.55	1.82	10.15	0.65%
7/27/09 19:45	20.2	45.1	50.5	3.08	7.62	2.03	2.60	1.24	11.28	0.08%
7/28/09 8:45	28.9	33.7	53.3	3.36	6.43	5.78	12.69	2.01	10.70	0.38%
7/28/09 14:15	27.2	36.3	68.7	5.19	NA	4.61	27.85	1.22	18.91	0.54%
7/28/09 19:45	19.9	51.9	60.9	4.61	7.88	2.13	2.72	0.67	14.02	0.06%
7/29/09 8:45	27.6	35.3	NA	3.58	8.89	4.36	12.37	1.14	19.40	0.35%
7/29/09 14:15	26.9	41.7	NA	8.37	13.70	5.52	18.56	2.01	17.09	0.22%
7/29/09 19:45	19.5	61.8	NA	5.28	5.95	2.32	1.56	1.51	14.02	0.03%
7/30/09 8:45	26.7	39.8	NA	9.80	11.06	4.01	8.81	1.52	22.57	0.09%
7/30/09 14:15	26.0	42.1	NA	4.63	12.99	3.72	9.26	2.06	25.11	0.20%
7/30/09 19:45	18.3	NA	NA	3.70	6.88	NA	1.83	NA	13.38	0.05%

[a] [H^+] is calculated from charge balance based on the IC measurements of [SO_4^{2-}], [NO_3^-], and [NH_4^+].
[b] "OS" represents organosulfate.

Table S3. Supporting data from BEACHON 2011 campaign.

Start Time[a]	average temperature (°C)	average RH (%)	average O_3 (ppb)	average organics (μg/m^3)	average [H^+][b] (nmol/m^3)	average MBO (ppb)	MBO OS[c] (ng/m^3)	DHIP[d] (ng/m^3)	IEPOX OS[c] (ng/m^3)	Isoprene tetrols[e]& triols[f] (ng/m^3)	Fraction of MBO OS in total organics
7/23/11 18:40	19.1	48.8	57.6	1.10	0.55	1.13	0.48	0.11	1.61	0.35	0.04%
8/1/11 17:10	15.0	73.5	42.5	1.26	1.10	0.54	0.27	0.08	1.06	0.52	0.02%
8/4/11 18:25	17.6	49.4	43.8	1.16	0.00	0.61	0.21	0.06	1.97	0.48	0.02%
8/7/11 19:45	17.5	39.3	45.9	1.52	0.58	0.88	0.29	0.03	1.05	0.36	0.02%
8/10/11 17:05	17.5	50.2	46.8	1.83	0.65	0.64	0.21	0.02	1.14	0.32	0.01%
8/16/11 18:15	18.2	47.1	39.3	1.30	0.58	0.84	0.00	0.11	0.09	0.48	0.00%

[a] The total sampling time for each sample is ~ 3 days (72 hrs); The total sampling volume for each sample is ~ 4320 m^3.
[b] [H^+] is calculated from charge balance based on the AMS data of [SO_4^{2-}], [NO_3^-], and [NH_4^+].
[c] "OS" represents organosulfate. Propyl sulfate was used as a surrogate standard for quantification.
[d] "DHIP" represents the 2,3-dihydroxyisopentanol measured from GC/EI-MS. *meso*-erythritol was used as a surrogate standard for quantification.
[e] "isoprene tetrols" represent the 2-methyltetrols measured from GC/EI-MS. *meso*-erythritol was used as a surrogate standard for quantification.
[f] "isoprene triols" represent the C5-alkenetriols measured from GC/EI-MS. *meso*-erythritol was used as a surrogate standard for quantification.

GC/EI-MS chemical analysis to measure DHIP:

Dried residues were trimethylsilylated by the addition of 100 μL of BSTFA + trimethylchlorosilane (99:1 (v/v), Supleco) and 50 μL of pyridine (Sigma-Aldrich, 98%, anhydrous), and the resultant mixture was then heated for 1 h at 70 ºC. SOA compounds that contain carboxyl and hydroxyl moieties are converted into volatile trimethylsilyl (TMS) derivatives that can be detected by GC/MS (Surratt et al., 2006). The details of the GC/MS technique and the operation procedures can be found in Zhang et al. (2011).

Table S4. Standard deviations of MBO mixing ratios from the investigated campaigns.

BEARPEX2007 Start Time	average MBO (ppb)	MBO std_dev (ppb)	BEARPEX2009 Start Time	average MBO (ppb)	MBO std_dev (ppb)	BEACHON2011 Start Time	average MBO (ppb)	MBO std_dev (ppb)
9/20/07 18:45	0.10	0.06	7/25/09 19:15	1.54	1.33	7/23/11 18:40	1.13	NA
9/21/07 7:45	0.25	0.06	7/26/09 8:45	4.47	0.72	8/1/11 17:10	0.54	0.32
9/21/07 13:15	0.40	0.02	7/26/09 14:15	6.59	2.35	8/4/11 18:25	0.61	0.17
9/21/07 18:45	0.11	0.00	7/26/09 19:45	1.99	1.71	8/7/11 19:45	0.88	0.40
9/22/07 7:45	0.18	NA	7/27/09 8:45	5.77	0.52	8/10/11 17:05	0.64	0.42
9/22/07 13:15	0.18	0.18	7/27/09 14:15	5.81	0.73	8/16/11 18:15	0.84	0.30
9/22/07 18:45	0.05	0.05	7/27/09 19:45	2.03	1.36			
9/23/07 7:45	0.08	0.02	7/28/09 8:45	5.78	0.38			
9/23/07 13:15	0.18	0.13	7/28/09 14:15	4.61	1.02			
9/23/07 18:45	0.05	0.03	7/28/09 19:45	2.13	1.88			
9/24/07 7:45	0.18	0.01	7/29/09 8:45	4.36	0.82			
9/24/07 13:15	0.28	0.03	7/29/09 14:15	5.52	1.76			
9/24/07 18:45	0.11	0.02	7/29/09 19:45	2.32	1.56			
9/25/07 7:45	0.37	NA	7/30/09 8:45	4.01	0.50			
9/25/07 13:15	0.40	NA	7/30/09 14:15	3.72	0.49			

Table S5. Available instrumentation uncertainties.

Measurement	Instrument Name	Chamber/Field	Uncertainty	Unit
Aerosol acidity	pH probe	EPA chamber	0.02[a]	pH
Organic carbon	semi-continuous EC-OC instrument	EPA chamber	1.5	µgC m^{-3}
NO_x	Chemiluminescent NOx monitor	UNC chamber	2± 0.3	ppb
O_3	UV photometric ozone monitor	UNC chamber	3± 0.5	ppb
MBO	GC/FID	UNC chamber	10	%
Particle volume	SMPS	UNC chamber	15[b]	%
Aerosol mass	HR-ToF-AMS	BEARPEX2007	0.04[c]	µg m^{-3}
Aerosol mass	FTIR	BEARPEX2009	20[d]	%
Inorganic mass	IC	BEARPEX2009	20	%
MBO	GC/FID NOAA	BEARPEX	See Table S4	ppb
MBO	GC/FID TAMU	BEARPEX	See Table S4	ppb
Aerosol mass	HR-ToF-AMS	BEACHON2011	30[e]	%
MBO	PTR-TOF-MS Ionicon Analytik GmbH[f]	BEACHON2011	15	%
MBO	PTR-TOF-MS U of Innsbruck[f]	BEACHON2011	15	%

[a] On the $[H^+]_{air}$ axis, the error bars denote the range in values due to the ± 0.02 pH unit uncertainty of the pH probe. They get larger as you move right because $[H^+]$ is a linear scale, but the pH measurement is a log scale. These values are consistent with what all the other experiments plotted would show if they were also given error bars on this axis (all experiments used comparable pH probes). On the OC axis, it is the usual standard deviation of the set of OC measurements averaged over the designated sampling period, converted into "% Change" space. These are pretty large on all MBO points because the "neutral" case that is used to normalize the OC values was relatively low, so even small standard deviations in total OC get inflated when converted into "% Change". All of the other experiments shown here would have smaller error bars on this axis because they would be normalizing with much higher starting OC values (by a factor of 5-10). Actual variability in the OC measurements was consistent across all experiments, with a standard deviation of about 1.5 µgC m^{-3}.

[b] Uncertainty of SMPS can be referred to Zhang et al., Effect of relative humidity on SOA formation from isoprene/NO photooxidation: enhancement of 2-methylglyceric acid and its corresponding oligoesters under dry conditions. *Atmos. Chem. Phys.* **2011**, *11*, 6411–6424.

[c] Uncertainty less than 0.04 µgm-3 for 1 minute data (refer to DeCarlo et al., Field-deployable, high-resolution, time-of-flight aerosol mass spectrometer. *Anal. Chem.* **2006**, *78*, 8281–8289).

[d] FTIR uncertainty refer to Russell, Aerosol organic-mass-to-organic-carbon ratio measurements. *Environ. Sci. Technol.* **2003**, *37*, 2982–2987.

[e] Refer to R. Bahreini et al., Organic aerosol formation in urban and industrial plumes near Houston and Dallas, TX. *Journal of Geophysical Research-Atmospheres* **2009**, *114*, D00F16, doi:10.1029/2008JD011493.

[f] Based on Poisson statistics and typical sensitivities for the NCAR (UIBK) PTR-TOF-MS of 50 (90) cps/ppbv we determined a precision of 0.8% (0.6%) for 1 ppbv and a 6 min time average. The accuracy was 15% for both instruments due to uncertainties of the calibration gas standard (5%) and the dilution system (10%). This leads to a typical LOD of 0.6 pptv (0.4 pptv) for an integration time of 6 minutes.

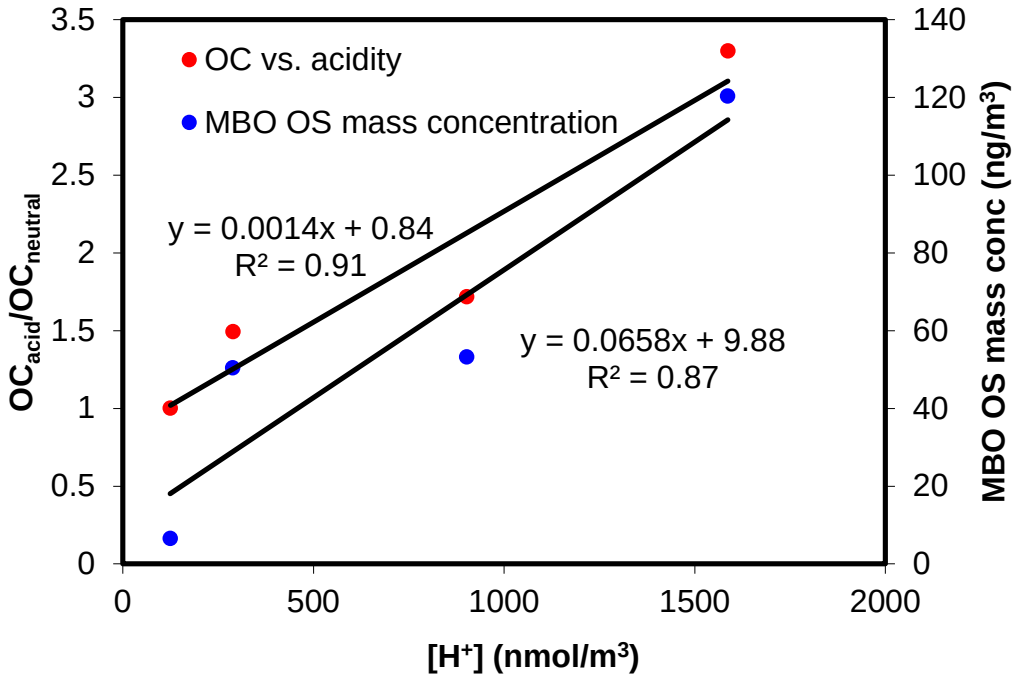

Figure S1. Correlation of the ratio of organic carbon (OC) concentration at elevated acidity relative to the neutral seed case and measured MBO organosulfate to measured aerosol acidity ($[H^+]_{air}$ nmol m^{-3}) from the EPA chamber experiments.

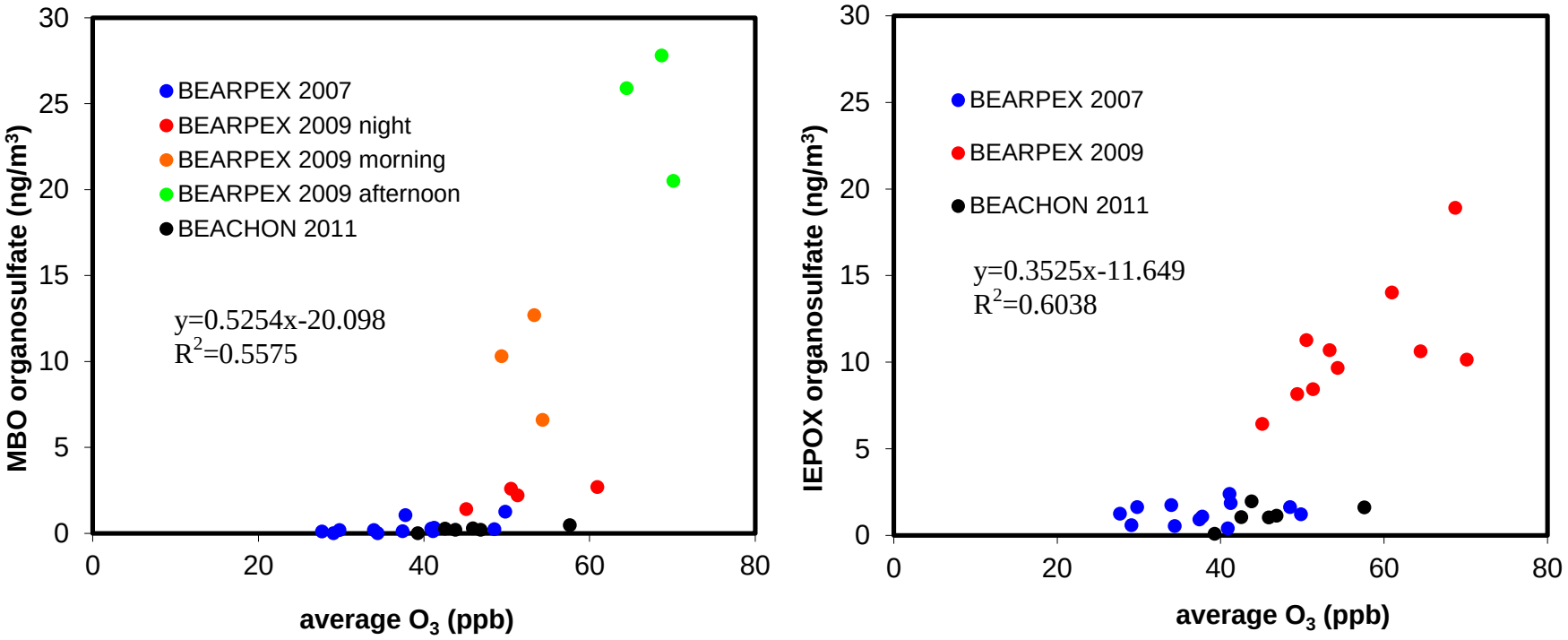

Figure S2. Correlations of MBO organosulfate (a) and IEPOX-derived organosulfate (b) mass concentrations to averaged O_3 from field measurements. The correlations suggest both ozone and organosulfates are secondary pollutants.

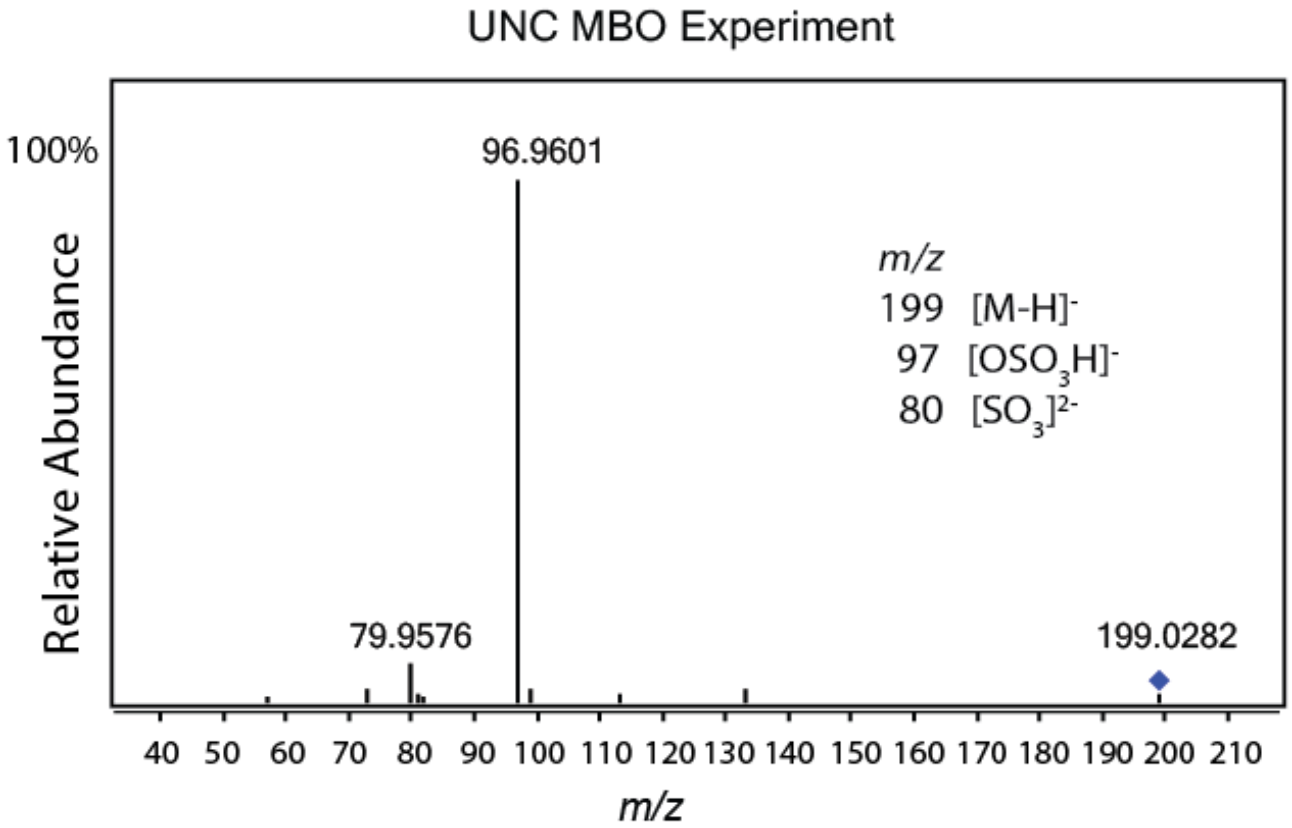

Figure S3. Tandem mass spectra (MS^2) of the MBO organosulfate (*m/z* 199) measured from the UNC high-NO chamber experiments.

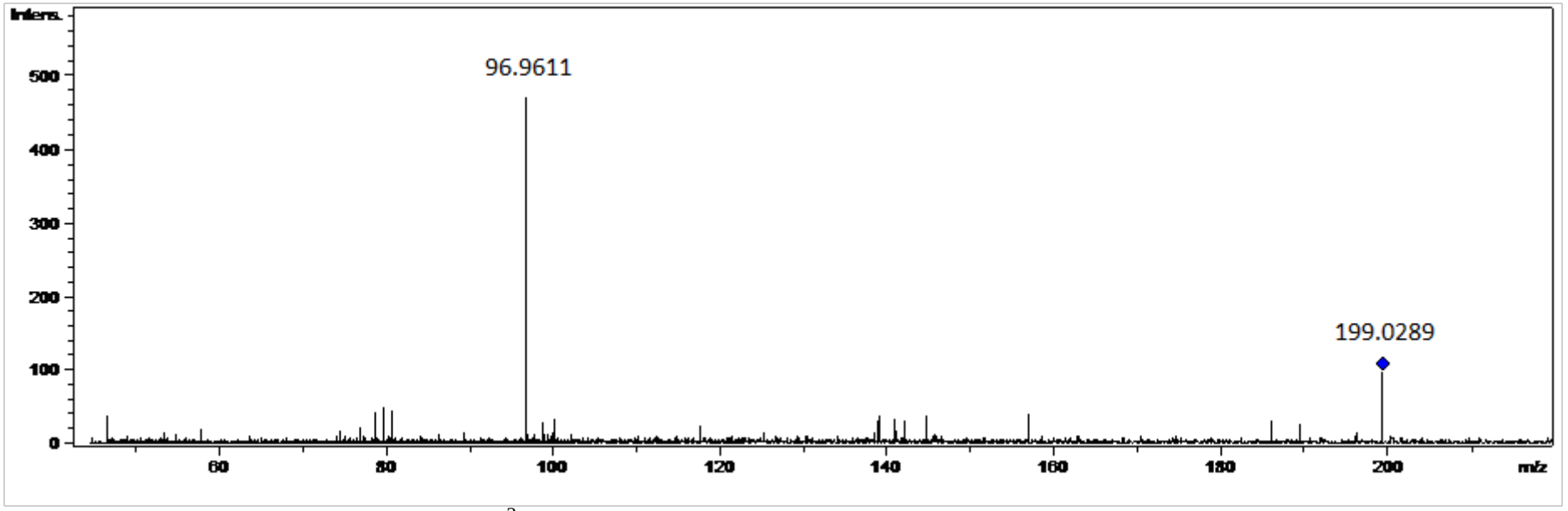

Figure S4. Tandem mass spectra (MS^2) of the MBO organosulfate (*m/z* 199) measured from the BEARPEX campaigns.

MBO intercalibration at BEARPEX

Measurements of MBO were made at 6.4m (NOAA, 2007) and 17.8m (TAMU, 2009). PTRMS measurements of the sum of MBO plus isoprene were made at five heights (1.5, 6.1, 9.3, 14.3 and 17.8m) through the canopy in both campaigns by the University of California, Berkeley (UCB). The diurnal profiles of MBO and isoprene were very different because MBO is locally emitted and isoprene is advected in from several hours upwind (Figure S5). MBO concentrations are dominant over isoprene in the early morning (Figure S5) when light and temperature driven emissions accumulate in the shallow boundary layer and transport from upwind is minimal. Figure S5 shows the comparison of MBO+isoprene (PTRMS) and MBO+isoprene (GC/MS or GC/FID) for the early morning (06:30 – 08:30, 2007; 07:00 – 10:00, 2009) and 2009 (TAMU) when MBO is dominant over isoprene. The comparable slopes of NOAA and TAMU versus UCB show that the MBO calibration scales are similar and that differences in the absolute observed concentrations are due to real variations driven by meteorological conditions between the two campaigns. The MBO+isoprene signal shows a strong vertical gradient through the canopy (Figure S6). This gradient is entirely driven by MBO and not isoprene as it is the local emitted species and this is supported by the absence of a gradient in the sum of methyl vinyl ketone and methacrolein (MVK+MACR), the first generation oxidation products of isoprene (Figure S6). Due to the strong gradient concentrations at 6.1m are 17.8m (Figure S6), this difference has not be taken into account in the concentrations reported here but would make the concentrations in 2009 approximately 1.5 times higher.

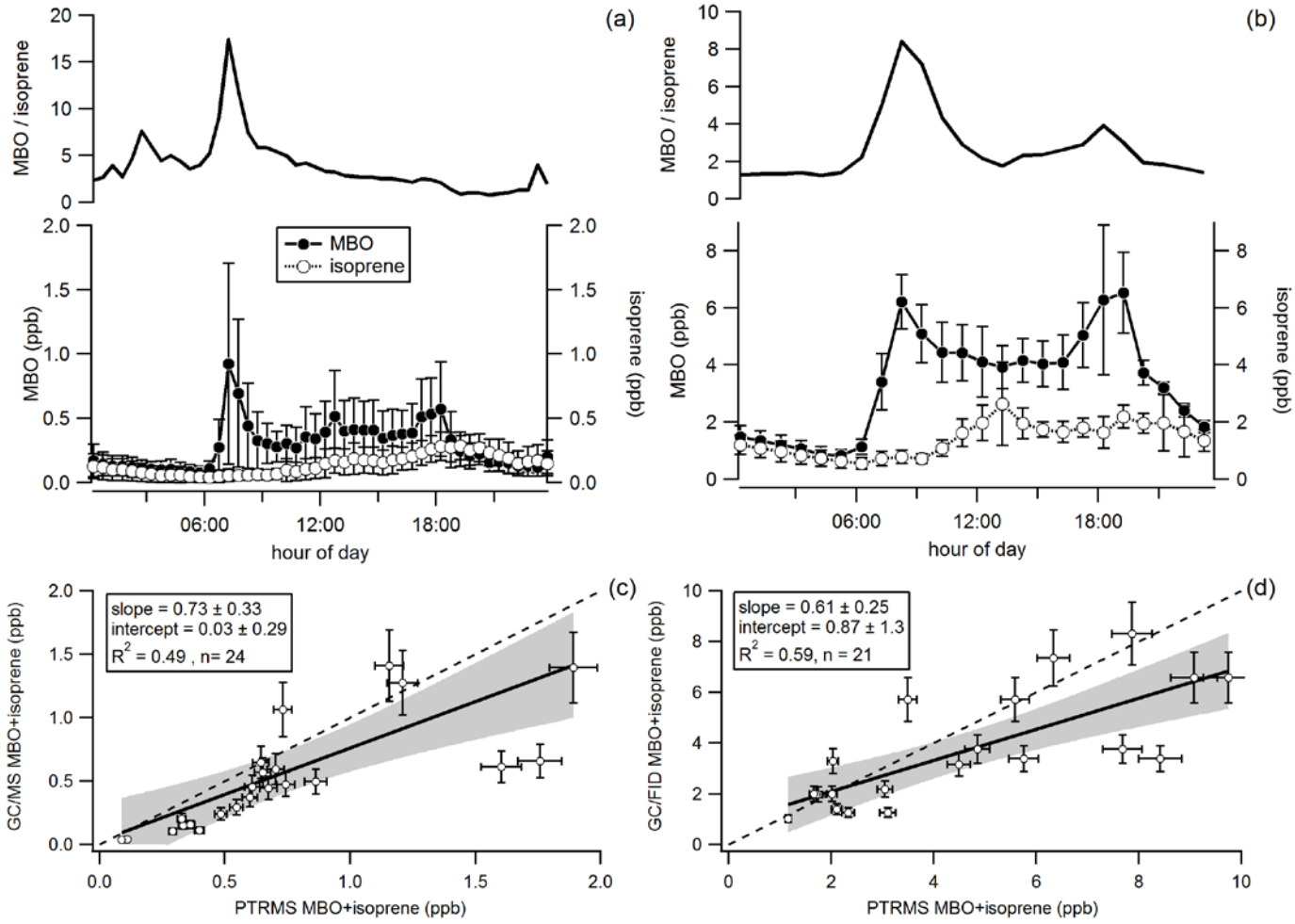

Figure S5. Diurnal variation of MBO, isoprene and the ratio of MBO to isoprene during (a) 2007 and (b) 2009. Comparison of the sum of MBO+isoprene in the early morning only measured by GC and PTRMS during (c) 2007 and (d) 2009.

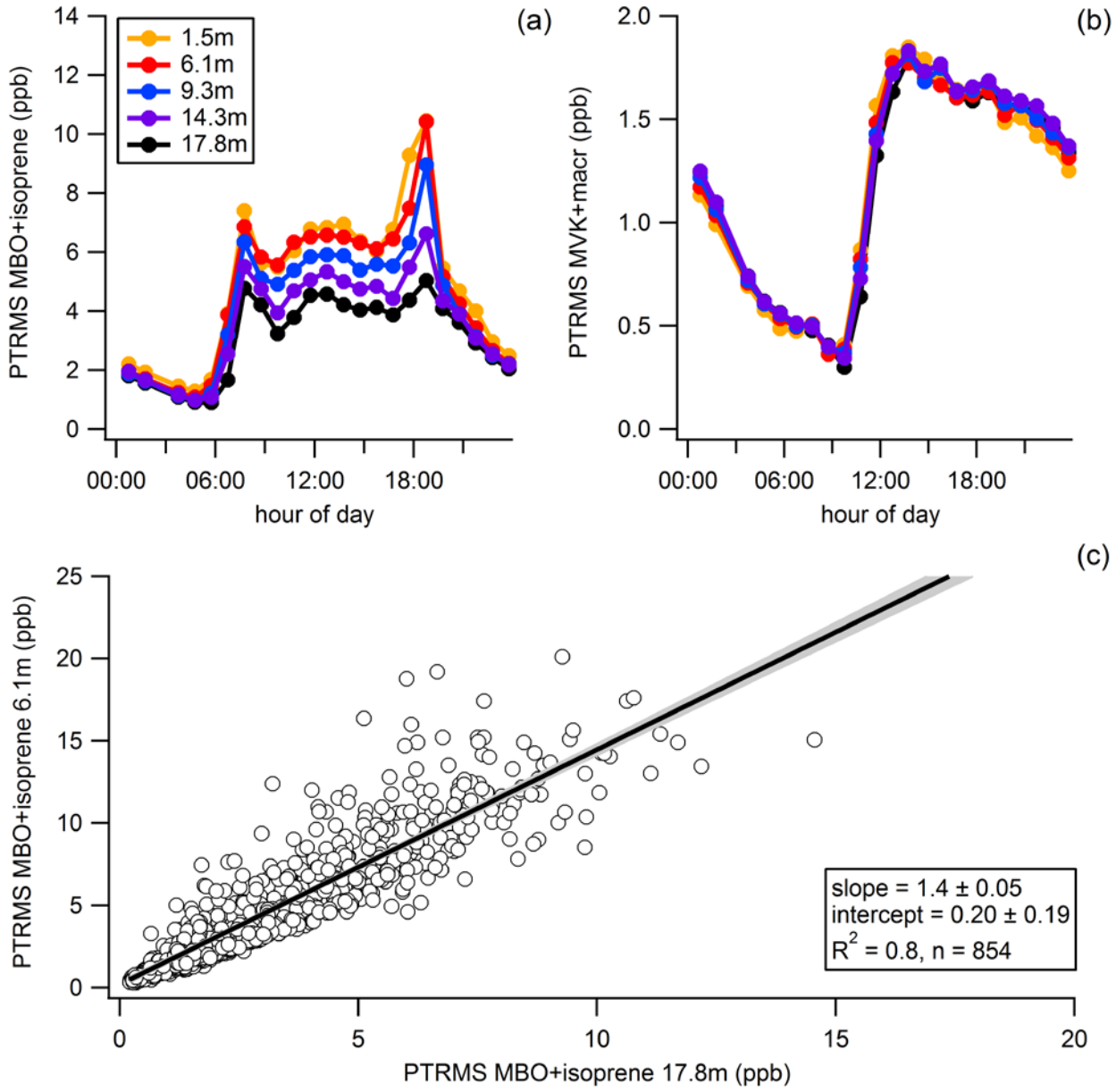

Figure S6. PTR-MS gradient measurements at 5 heights (1.5, 6.1, 9.3, 14.3 and 17.8m) in 2009 for (a) MBO+isoprene and (b) methyl vinyl ketone+methacrolien (MVK+MACR). Comparison of MBO+isoprene concentrations at 17.8 and 6.1m heights in 2009.

MBO intercalibration at BEACHON-RoMBAS

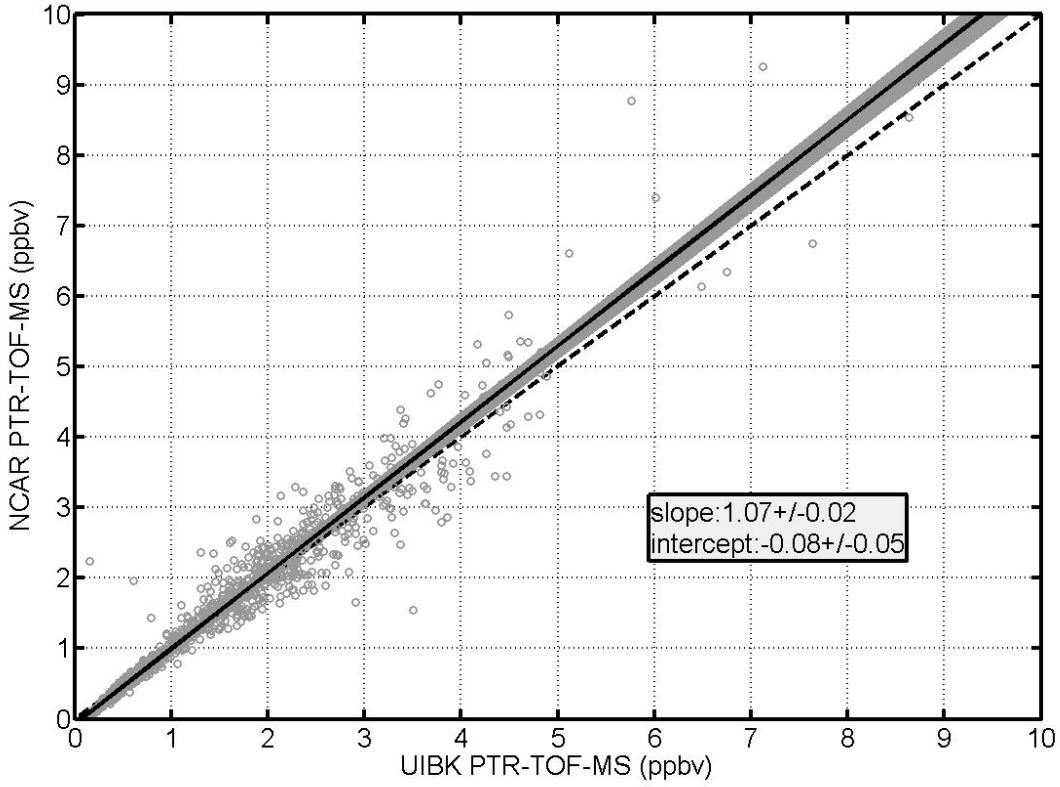

Figure S7. Intercomparison of the NCAR and UIBK PTR-TOF-MS during the BEACHON ROMBAS field campaign in summer 2011.